



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

0 306 183
A2

12

EUROPEAN PATENT APPLICATION

21 Application number: **88307673.9**

51 Int. Cl.4: **G01N 27/12**

22 Date of filing: **18.08.88**

30 Priority: **31.08.87 JP 217103/87**

43 Date of publication of application:
08.03.89 Bulletin 89/10

84 Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

71 Applicant: **JUNKOSHA CO. LTD.**
25-25, Miyasaka 2-chome
Setagaya-ku Tokyo 156(JP)

72 Inventor: **Ishikawa, Tazuru**
322 Umahikizawa Hitaka-machi
Iruma-gun Saitama(JP)
Inventor: **Sato, Yoshiaki**
202 Forble-Sakae, 350-7 Kawadera
Hanno-shi Saitama(JP)

74 Representative: **Taylor, Derek George et al**
Mathisen, Macara & Co. The Coach House
6-8 Swakeleys Road
Ickenham Uxbridge UB10 8BZ(GB)

54 Oil leakage sensor.

57 An oil leakage sensor comprises a sensor element formed by a plurality of electrical conductors contained within and separated from each other by a continuously porous polytetrafluoroethylene PTFE material containing from 15 to 40 weight percent carbon particles, the carbon particles having irregular shapes and average diameter between 10 and 30 millimicrons, at least a portion of the exterior surfaces of the carbon particles being exposed at the pore walls of the PTFE and extending into the pores. The porous PTFE material is preferably obtained by stretching an extruded, unsintered PTFE film containing the carbon particles, after removal of lubricant, to a draw ratio of 1.5 times or less. The sensor element, in use, is connected between electrodes which, in turn, are connected to an alarm device. Preferably, the sensor element is connected to elongate electrodes (wires) such that the direction of stretch of the material is aligned with the lengthwise direction of electrodes.

EP 0 306 183 A2

OIL LEAKAGE SENSOR

The present invention relates to an oil leakage sensor for detecting leakage of oil on to a water surface by means of a change in electrical resistance.

A conventional oil leakage sensor comprises an element in which two conductors are separated by a polytetrafluoroethylene film containing carbon particles. When oil leaks on to the surface of water in which this sensor element is installed, the oil permeates the areas between the carbon particles inside the resin, and lowers conductivity arising from the tunnel effect. This causes a change in the electrical resistance value of the sensor element, and the oil leakage is detected as a result of this change in electrical resistance.

In the case of the above mentioned conventional sensor element, the PTFE is unsatisfactory in terms of permeability to high-viscosity oils such as heavy oils, especially grade C heavy oils, and vegetable oils. Furthermore, most of the carbon particles are surrounded by PTFE. As a result, the leaking oil does not achieve sufficient contact with the carbon particles. Consequently, the change in the electrical resistance value of the sensor element at the time of oil leakage is small, so that the oil leakage detection sensitivity is unsatisfactory.

According to the present invention there is provided an oil leakage sensor comprising a plurality of electrical conductors contained within and separated from each other by a continuously porous, stretched polytetrafluoroethylene (PTFE) material containing from 15 to 40 weight percent carbon particles, said carbon particles having irregular shapes and an average diameter between 10 and 30 millimicrons, at least a portion of the exterior surfaces of the carbon particles being exposed at the pore walls of the PTFE and extending into said pores.

In a preferred embodiment the porous extruded PTFE film containing the carbon particles has been stretched, after removal of lubricant, to an extent of 1.5 times or less its unstretched length. The sensor element in use is connected by wires to resistance metering apparatus. The element is preferably connected to the metering apparatus such that the direction of stretch of the material is aligned with the direction along the material in which resistance is measured.

An embodiment of the present invention will now be particularly described, by way of example, with reference to the accompanying drawings in which:-

Figure 1 is a diagrammatic representation of the composite material used in the sensor element, under high magnification;

Figure 2 is an oblique view of one embodiment of the oil leakage sensor element connected between two wires;

Figure 3 is a schematic view of the material used in the sensor in tape form wound about a core and which is referred to in the examples discussed below;

Figure 4 is an oblique view of the tape material used in the examples;

Figure 5 is a schematic diagram of the experiments referred to in the examples, and

Figure 6 is a graph showing the results of the experiments.

The oil leakage sensor element is characterised by the fact that multiple conductors are separated from each other by a material which is formed by impregnating 15 to 40 weight percent carbon particles, which are 10 to 30 millimicrons in diameter and which have irregular surfaces so that their surface area is increased, into a continuously porous polytetrafluoroethylene, and in which the exterior surfaces of the aforementioned carbon particles are exposed at the pore walls of the PTFE.

Polytetrafluoroethylene containing a relatively large quantity of carbon particles has an electrical conduction mechanism which depends on three-dimensional chains of contacting carbon particles. In the present invention, since the exterior surfaces of the carbon particles are exposed at the pore walls of the continuously porous resin, oil components can easily adhere to the exterior surfaces of the carbon particles following permeation of the resin by a high-viscosity oil. The exterior surfaces of the carbon particles are irregular so that the effective surface area of the carbon particles is increased. As a result, oil is securely adsorbed on the carbon particles and the conductivity of the carbon particles themselves drops as a result of oil absorption by the resin.

In Figure 1, polytetrafluoroethylene PTFE 1 constitutes a composite material 4 which contains carbon particles 2, and which has numerous pores 3 that connect with the outside of the material. Such pores 3 are formed by drawing PTFE 1 which contains carbon particles 2 by known techniques. As a result, the composite material 4 is a stretched, porous PTFE 1 which contains carbon particles 2 and has pores 3 therein.

The carbon particles 2 are small particles with diameters of 10 to 30 millimicrons. These particles have irregular structures, with numerous indentations and projections formed on the surfaces of the particles, so that the effective surface area of the particles is increased. The concentration of such carbon particles 2 in the PTFE 1 is 15 to 40 weight

percent. Furthermore, relatively large pores 3 are formed by stretching this PTFE, so that numerous carbon particles 2 are exposed through the walls and inside the pores 3. A portion of the carbon particles are in contact with each other, so that the composite material 4 is electrically conductive.

The drawing of the PTFE 1 is performed at a draw ratio of 1.5 times or less. If the drawing exceeds this draw ratio, there is a danger that the drawing will damage the water resistance of the material 4. Accordingly, drawing at a draw ratio of approximately 1.2 to 1.4 times is desirable in order to maintain the aforementioned water resistance and at the same time form sufficient pores 3. In the case of drawing at a draw ratio of 1.3 times, the average diameter of the pores 3 in the resulting drawn PTFE will be approximately 0.5 micrometers (microns).

The oil leakage sensor element is constructed by connecting a plurality of conductors 5 by means of the material 4 as shown in Figure 2. The composite material 4 used here has the form of a tape. The composite material 4 could also have a greater thickness, or could take the form of a cable. In Figure 2, two conductors 5 are connected by the aforementioned material 4. It would also be possible to construct an oil leakage sensor element in which three or more conductors 5 are connected by the composite material 4.

This oil leakage sensor element is installed so that the composite material 4 is positioned at the surface of a quantity of water, and current is caused to flow between the conductors 5. Leaking oil is detected by a change in the electrical resistance value of the sensor element. Specifically, the composite material 4 is positioned at or near the water surface. The pores 3 in the material are extremely small and the material 4 itself is water-repellent. Accordingly, when no leaking oil is present, there is no invasion of the interiors of the pores 3 by water, and current flows between the conductors 5 in proportion to the quantity of carbon particles 2 contained in the material 4. At such time, the electrical resistance value between the conductors 5 is relatively low.

When oil leakage occurs, the oil spreads over the surface of the water, and readily permeates the material 4 through the pores 3. This oil adheres to the surfaces of the carbon particles 2 which are exposed at the walls of the pores 3. Because the surfaces of the carbon particles 2 have an increased area due to the surface irregularities, the oil is securely adsorbed on the carbon particles 2. As a result, the carbon particles swell and increase in electrical resistance. Since the flow of current between the conductors 5 is achieved only through the carbon particles 2, the electrical resistance value between the conductors 5 is increased.

Because the surface area of the carbon particles 2 is increased by the formation of indentations and projections on the surfaces of the particles, the area of contact between the carbon particles 2 and the PTFE 1 is also increased. Accordingly, the carbon particles 2 which are exposed at the walls of the pores 3 are securely held by the PTFE 1 even in configurations where the particles are only partially embedded in the PTFE, or where projecting portions of the particles are stuck into the PTFE 1. As a result, the element has good durability, i.e., the carbon particles 2 will not fall out of the pores 3 even in long-term use.

Experiments which were performed in order to confirm the effect of making the PTFE 1 porous will be described below.

The carbon particles used were furnace-type carbon particles. Their commercial names are MA600, manufactured by Mitsubishi Kasei Kogyo K.K. and PT90, manufactured by Tokai Carbon K.K. These particles were separately mixed with a polytetrafluoroethylene fine powder, extruded, dried and the resulting samples were drawn to produce porous tapes. Figure 3 indicates one of these tapes 6 wound about a core 10. The tape 6 was drawn in the direction of length. Because it was conceivable that the electrical resistance might differ according to the direction of drawing, two different types of samples were cut out of the respective tapes 6, i.e., longitudinal samples, indicated by A in Figure 3, cut along the direction of length (draw) of the tape 6, and lateral samples, indicated by B in Figure 3, cut along the direction of width of the tape 6.

Example 1

A first sample was an undrawn longitudinal (A) type sample in which 12 weight percent MA600 was mixed with the polytetrafluoroethylene.

Example II

This sample was an undrawn longitudinal A type sample in which 12 weight percent PT90 (described above) was mixed with polytetrafluoroethylene.

Example III

This sample was an undrawn lateral (B) type sample in which 12 weight percent PT90 was mixed with polytetrafluoroethylene.

Example IV

This sample was a longitudinal (A) type sample made porous by drawing to a draw ratio of 1.4 times, in which 30 weight percent PT90 was mixed with the polytetrafluoroethylene.

Example V

This sample was a lateral (B) type sample made porous by drawing to a draw ratio of 1.4 times, in which 30 weight percent PT90 was mixed with polytetrafluoroethylene.

Example VI

This sample was a longitudinal A type sample made porous by drawing to a draw ratio of 1.4 times, in which 40 weight percent MA600 was mixed with polytetrafluoroethylene.

Example VII

This sample was a lateral (B) type sample made porous by drawing to a draw ratio of 1.4 times, in which 40 weight percent MA600 was mixed with polytetrafluoroethylene.

Figure 4 illustrates the sample tapes 4. The ends of each sample material 4 were folded in the direction of width, and were separately clamped by clips 7 as shown in Figure 5. These clips 7 were connected to a digital multipurpose-meter 8 which measured electrical resistance. Each sample material 4 was suspended in a U-form, and an area 4a with a height of 10mm from the bottom of the 'U' was immersed in grade C heavy oil. The grade C heavy oil was heated to a temperature of approximately 50 °C., and the change in electrical resistance was recorded every 10 seconds for each sample.

A polytetrafluoroethylene sheer 12 was interposed between the left and right portions of each U-form sample material 4 above the surface of the oil so that the legs of the "U" portions would not contact each other and short circuit.

Figure 6 shows the rate of change in electrical resistance $\Delta R/R_0$ measured for each of the samples 1 through VII from the time of initial immersion in the grade C heavy oil. The symbols I through VII in Figure 6 indicate the rates of change in electrical resistance for the corresponding samples I through VII mentioned above.

It is seen from Figure 6 that the rate of change in electrical resistance is increased, and that sensitivity is improved, in cases where the poly-

tetrafluoroethylene is made porous by drawing, compared to cases where the polytetrafluoroethylene is not made porous by drawing. It can also be seen that in the case of the same material, samples cut along the direction of drawing, type A in Figure 3, show additional improved sensitivity.

As described above, the present invention improves the permeability of an oil leakage sensor element by high-viscosity oils, and also increases the contact of such oils with the carbon particles. As a result, the rate of change in the electrical resistance value of the oil leakage sensor element of the present invention is substantially increased, and the sensitivity of the element can be improved approximately eightfold as shown by the above experiments.

Claims

1. An oil leakage sensor characterised by a plurality of electrical conductors contained within and separated from each other by a continuously porous, stretched polytetrafluoroethylene PTFE material containing from 15 to 40 weight percent carbon particles, said carbon particles having irregular shapes and an average diameter between 10 and 30 millimicrons, at least a portion of the exterior surfaces of the carbon particles being exposed at the pore walls of the PTFE and extending into said pores.

2. A sensor according to claim 1 characterised in that said porous, stretched PTFE material is an extruded PTFE film containing said carbon particles which has been stretched, after removal of lubricant, to an extent of 1.5 times or less its unstretched length.

3. A sensor according to claim 1 further characterised in that resistance metering apparatus connected to said conductors.

4. A sensor according to claim 3 characterised in that said conductors are connected to said material such that the direction of stretch of said material is aligned with the direction along the material in which resistance is measured.

5. A sensor according to claim 2 characterised in that said material is stretched to an extent of 1.2 to 1.4 times its unstretched length.

6. A sensor according to claim 5 characterised in that said material has been stretched to an extent of 1.3 times its unstretched length.

Fig. 1.

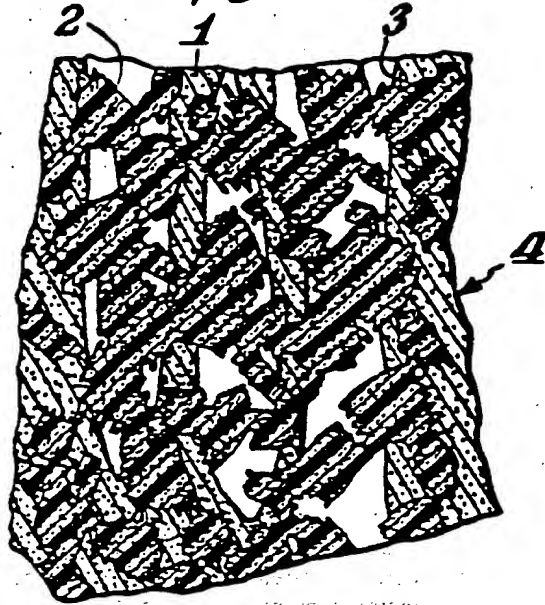


Fig. 4.

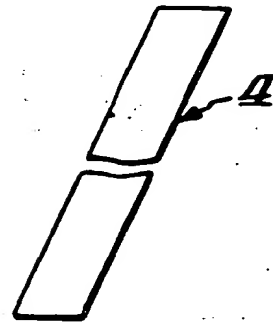


Fig. 2.

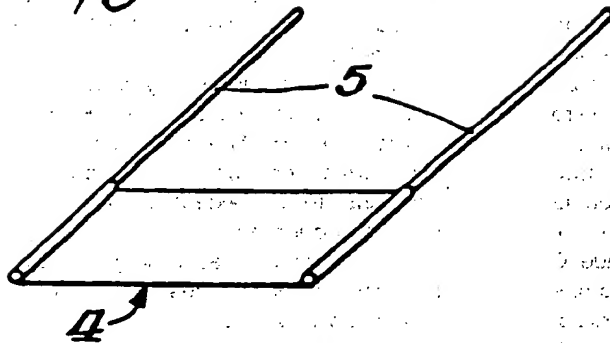


Fig. 5.

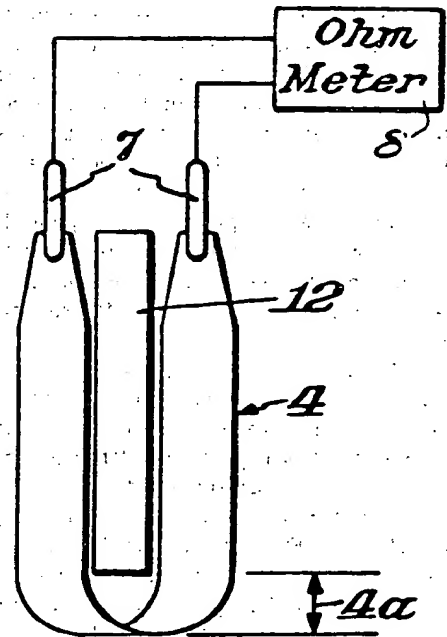
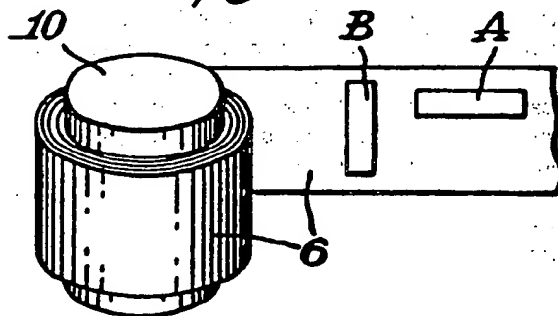
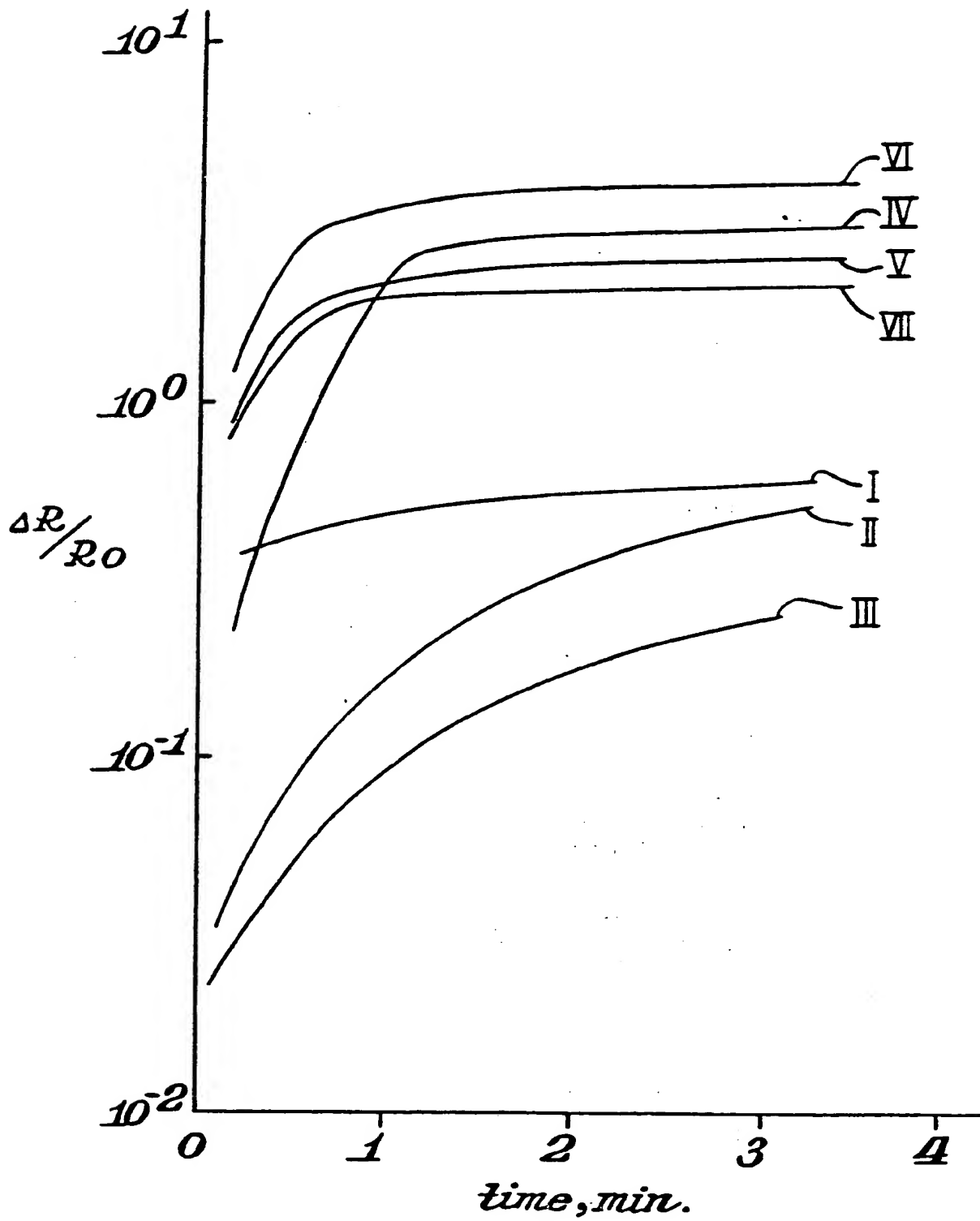


Fig. 3.



*Fig. 6.*

12

EUROPEAN PATENT APPLICATION

21 Application number: **88307673.9**

51 Int. Cl.5: **G01N 27/12 , G01M 3/04**

22 Date of filing: **18.08.88**

30 Priority: **31.08.87 JP 217103/87**

43 Date of publication of application:
08.03.89 Bulletin 89/10

84 Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

88 Date of deferred publication of the search report:
09.05.90 Bulletin 90/19

71 Applicant: **JUNKOSHA CO. LTD.**
25-25, Miyasaka 2-chome
Setagaya-ku Tokyo 156(JP)

72 Inventor: **Ishikawa, Tazuru**
322 Umahikizawa Hitaka-machi
Iruma-gun Saitama(JP)
Inventor: **Sato, Yoshiaki**
202 Forble-Sakae, 350-7 Kawadera
Hanno-shi Saitama(JP)

74 Representative: **Taylor, Derek George et al**
Mathisen, Macara & Co. The Coach House
6-8 Swakeleys Road
Ickenham Uxbridge UB10 8BZ(GB)

54 **Oil leakage sensor.**

57 An oil leakage sensor comprises a sensor element formed by a plurality of electrical conductors contained within and separated from each other by a continuously porous polytetrafluoroethylene PTFE material containing from 15 to 40 weight percent carbon particles, the carbon particles having irregular shapes and average diameter between 10 and 30 millimicrons, at least a portion of the exterior surfaces of the carbon particles being exposed at the pore walls of the PTFE and extending into the pores. The porous PTFE material is preferably obtained by stretching an extruded, unsintered PTFE film containing the carbon particles, after removal of lubricant, to a draw ratio of 1.5 times or less. The sensor element, in use, is connected between electrodes which, in turn, are connected to an alarm device. Preferably, the sensor element is connected to elongate electrodes (wires) such that the direction of stretch of the material is aligned with the lengthwise direction of electrodes.

EP 0 306 183 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 30 7673

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	DE-A-2 822 769 (JUNKOSHA CO. LTD) * Entire document * ---	1-6	G 01 N 27/12 G 01 M 3/04
E	PATENT ABSTRACTS OF JAPAN, vol. 13, no. 152 (P-856)[3500], 13th April 1989; & JP-A-63 314 451 (JUNKOSHA CO. LTD) 22-12-1988 * Abstract; figure * ---	1-6	
E	EP-A-0 298 463 (JUNKOSHA CO. LTD) * Column 3, line 6 - column 4, line 31; figures; claims * ---	1,2,3	
A	FR-A-2 204 304 (P. BENNO) * Entire document * ---	1-6	
A	DE-A-3 441 924 (JUNKOSHA CO. LTD) * Entire document * -----	1-6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			G 01 N 27/00 G 01 M 3/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07-02-1990	Examiner BROCK T.J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P0401)